AN INVESTIGATION OF THE SOURCES AND TRANSPORT

OF NONPOINT SOURCE NUTRIENTS IN THE

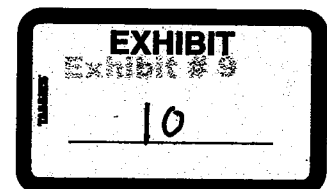ILLINOIS RIVER BASIN IN OKLAHOMA

AND ARKANSAS

By

DAVID R. GADE

Bachelor of Science
University of Wisconsin - Stevens Point
Stevens Point, Wisconsin
1981

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1990

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
May, 1998

AN INVESTIGATION OF THE SOURCES AND TRANSPORT

OF NONPOINT SOURCE NUTRIENTS IN THE

ILLINOIS RIVER BASIN IN OKLAHOMA

AND ARKANSAS

Thesis Approved:

_____

Thesis Advisor

_____

_____

_____

Dean of the Graduate College

ACKNOWLEGEMENTS

I wish to express my sincere thanks and appreciation to all those who assisted me in this project. Dr. Sterling Burks formed the foundation of my graduate work at Oklahoma State University and directed me to studies of the Illinois River and eventually this topic. Dr. Daniel Storm, my major advisor, has been a patient and insightful supervisor of this project, without whom I could not have completed this research. I also wish to thank the other members of my committee, Dr. Smolen, Dr. Claypool, and Dr. Lawler, for their patience, insightful comments, and assistance in completing this study. I am indebted to graduate students and employees at the OSU-Water Quality Research Laboratory who collected information and data which I was able to use in my research. Various important details of this research were performed by numerous faculty members and employees of the Biosystems and Agricultural Engineering Department, and the Agronomy Department at Oklahoma State University, and I owe them thanks as well.

Finally, I wish to express my sincerest thanks to my wife, Mary, and our children, Emma and Noah, for their patience and unconditional love throughout this process.

iii

TABLE OF CONTENTS

LIST OF TABLES

Table   Page

Table   Page

Table   Page

Table   Page

Table   Page

LIST OF FIGURES

Figure   Page

Figure   Page

Figure   Page

Figure   Page

Figure   Page

CHAPTER I

INTRODUCTION

Nitrogen and phosphorus are considered by most limnologists to be the nutrients most commonly limiting algal growth in surface waters. Quantities of these plant nutrients that are available for transport to surface waters are influenced by anthropogenic activities. When these nutrients are present in surface waters in excessive quantities, algal populations tend to experience seasonal growth blooms that may detract from aesthetic characteristics of streams and lakes, and contribute to accelerated eutrophication of water bodies.

Watersheds are ecosystems composed of a mosaic of different land uses connected by a network of streams. In-stream conditions are determined by processes occurring within the watershed and cannot be isolated from or manipulated independent of the watershed. In this study, the stream network of interest drains into a single large reservoir, and the water quality in the reservoir is then directly related to conditions and processes occurring within the watershed. An evaluation of the movement of certain pollutants, such as the nutrients nitrogen and phosphorus, from the watershed to the reservoir should include information about land uses, soil types, geology, topography, precipitation, and surface drainage patterns. Geographic information systems

(GIS) allow for the inclusion of all these aspects in an overall model of nutrient transport.

The Illinois River Basin in Oklahoma and Arkansas has been the subject of numerous water quality studies, primarily concerned with factors affecting water quality in the scenic river portions of the Illinois River in Oklahoma, and nutrient loading to Lake Tenkiller. The state (Oklahoma) scenic river status of the Illinois River from Watts to Tahlequah, and the tributaries Flint Creek and Baron Fork Creek, legislates that these designated stream sections receive special attention regarding increases in levels of pollution.

The area including the Illinois River Basin has experienced significant economic development in the past two decades. Changes that likely have affected the water quality of the Illinois River and Lake Tenkiller include expanding urban development and an increase in confined animal production. While assessing blame on any particular industry or urban center within the basin without a definitive study is difficult, and perhaps politically unwise, there is evidence that an expanding population and a booming poultry industry are significant contributors to the increasing levels of nutrients transported via the Illinois River and its tributaries to Lake Tenkiller. A 1989 Soil Conservation Service (SCS, 1989) inventory estimated more than 93,400,000 birds are raised in the basin per year producing approximately 366,000,000 kilograms of manure per year. Estimated nitrogen (N) and phosphorus (P) quantities in this manure are 4,680,000 kilograms N per year and 1,400,000 kilograms P per year. These nutrients are used to fertilize pasture and crop lands in the basin to promote the

3

growth of forage for cattle. Significant fractions of this fertilizer are likely not incorporated into herbaceous or animal biomass and are susceptible to transport into surface streams during runoff events, and leaching, especially for nitrogen, to ground water.

Lake Tenkiller, the ultimate receptacle of nutrients flowing into the Illinois River and its tributaries, has displayed evidence of accelerated eutrophication over the past twenty years. The influx of the nitrogen and phosphorus provide essential nutrients for the growth of algal populations. Dense spring algal blooms have been observed in the reservoir in recent years and, during periods of summer stratification, the hypolimnion of the reservoir has become anoxic. Continued input of these nutrients will likely exacerbate problems already observed and contribute to decreased aesthetic and water quality in the reservoir.

The objectives of the study were to:

1)   identify the areas and land uses which are most highly correlated with the transport of the nutrients nitrogen and phosphorus from the watershed to tributaries, the Illinois River, and Lake Tenkiller;

2)   quantify the amounts of nitrogen and phosphorus coming from point and nonpoint sources using a comprehensive nonpoint source hydrologic water quality model; and,

3)   determine the potential beneficial effects, in terms of

4

reduced nutrient loading, of specific reductions of nonpoint

nutrient quantities within the basin.

A continuous simulation phosphorus transport model called SIMPLE

(Sabbagh et al., 1995) developed by the Biosystems and Agricultural

Engineering Department at Oklahoma State University, interfaced with the GIS

GRASS 4.0 (CERL, 1988), was used to model nonpoint phosphorus transport

from subwatersheds of the Illinois River Basin to the Illinois River and its

tributaries. The model incorporates the SCS Curve Number Method for

determination of runoff, the Revised Universal Soil Loss Equation for the

calculation of sediment loss, a linear isotherm to simulate the desorption of

phosphorus in the soil matrix, and a mass balance accounting of the soil

phosphorus. GIS data layers include topographical data from USGS 1:24,000

scale quadrangle maps, soil types and characteristics from county soil surveys,

land uses derived from aerial photography, and animal densities and the

locations of poultry houses.

This model was developed for the determination of long-term phosphorus

loading. SIMPLE was used to estimate nonpoint source phosphorus export from

the watershed to the receiving stream. This model was applied to subbasins

defined by a Digital Terrain Model (DTM), a component of the SIMPLE Model,

comprising the total Illinois River Basin including Lake Tenkiller.

Outputs from runs of the phosphorus transport model were routed through

a riverine water quality model, QUAL2EU (Brown and Barnwell, 1987),

incorporating uncertainty analysis, which simulates the fate of nutrients as they

move downstream to Lake Tenkiller.

The SIMPLE model does not simulate the transport of nitrogen, but nitrogen is a nutrient of interest to limnologists concerned with the effect of nutrient loads on streams and lakes (and reservoirs). Thus, unit area loadings for nitrogen, based on land uses, were developed based on literature values to estimate total nitrogen export from the defined subbasins. Unit area loads are simple estimates expressing pollution generation per unit area and time unit for each typical land use (Novotny, 1986). This method was used to estimate nitrogen export from subbasins in the watershed for use as QUAL2EU input. Results of the modeling effort were compared with nutrient loading quantities developed from historical discharge and concentration data measured at water quality monitoring stations in the Illinois River Basin.

The SIMPLE model, with its GIS interface, was used to identify those areas in the basin that are most highly correlated with phosphorus transport based on soil characteristics, land uses, slope, and fertilizer application. The SIMPLE model and unit area loadings were used to quantify nutrient loads available for transport to Lake Tenkiller. The QUAL2EU model was used to route and quantify point and nonpoint nutrient loads to Lake Tenkiller. The QUAL2EU model offers uncertainty analysis in the form of Monte Carlo simulations. These were employed to estimate the frequency distributions of nutrient concentrations and loads at specific locations on the Illinois River and its tributaries, and the upper portion of Lake Tenkiller, based on variable nutrient concentrations and stream discharge.

6

I analyzed historical water quality data to determine annual average nutrient concentrations and loads, temporal trends for nutrient concentrations and loads, and estimates of the sources of nutrients reaching the headwaters of Lake Tenkiller. These results, based on historical data, were compared with the modeled transport of nutrients down to the headwaters of Lake Tenkiller. Estimated reductions of nutrient transport to Lake Tenkiller due to reductions in nonpoint source inputs of nutrients were quantified. Trophic state indices were used to estimate the trophic state of the headwaters of Lake Tenkiller under simulated average annual conditions and with 25 and 50 percent reductions in nonpoint source inputs.

Chapter II is a brief description of the study area, the Illinois River Basin in Oklahoma and Arkansas. Chapter III is a review of literature applicable to this study touching on water quality in the Illinois River Basin, phosphorus and nitrogen properties and characteristics, nutrient unit area loading methods, characteristics of animal wastes, nonpoint source pollution, and nonpoint source pollution modeling.

Chapter IV outlines the methodology followed concerning data gathering, and analysis for automatic sampling selected stream sites, historical data, SIMPLE input data sets, and QUAL2EU data sets. Chapter V gives results of automatic sampling, analysis of historical water quality data, SIMPLE runs on the Illinois River Basin, and results of QUAL2EU model runs.

Chapter VI is a discussion of the results with comments about management practices, and, Chapter VII offers some concluding remarks.

CHAPTER II

DESCRIPTION OF THE STUDY AREA

The Illinois River above 650 feet mean sea level, was designated as a state "scenic river" in 1969 by an act of the Oklahoma Legislature in an attempt to preserve and protect the qualities of the river that make it unique and attractive. The Oklahoma Scenic Rivers Act of 1969 states " . . . some of the free-flowing streams and rivers of Oklahoma possess such unique natural scenic beauty, water conservation, fish, wildlife and outdoor recreational values of present and future benefit to the people of the state that it is the policy of the Legislature to preserve these areas for the benefit of the people of Oklahoma" (OK Statutes, Title 82 O.S. Supp. 1981, Sec. 1451).

A supplement to the Scenic Rivers Act in 1981 designated portions of two major tributaries of the Illinois River, Flint Creek and Baron Fork Creek, as state scenic rivers as well. The act provides that designated scenic river areas be preserved in their free-flowing forms, and directs and authorizes the Director of the Oklahoma Water Resources Board and other state water pollution control agencies to assist in preventing and eliminating pollution of waters within a scenic river area (OK Statutes, Title 82 O. S. Supp. 1981, Sec. 1451).

8

An Act of the Oklahoma Legislature in 1977 provided for the formation of theOklahoma Scenic Rivers Commission with responsibility to carry out the intended purpose of the Oklahoma Scenic Rivers Act. The Illinois River has been, and continues to be, a premier tourist attraction of the state, drawing thousands of people annually to northeastern Oklahoma. The region offers abundant camping, hunting and fishing, and canoeing opportunities in a setting that is unique to the Ozark region.

The Oklahoma Water Quality Standards of 1988 (OWRB, 1989) list beneficial uses of the scenic river portions of the Illinois River, Flint Creek, and Baron Fork Creek as: 1) public and private water supply, 2) smallmouth bass fishery, 3) primary recreation, 4) agriculture (non-irrigation), and 5) aesthetics. These standards list no numerical standards for nutrient concentrations. However, an Anti-Degradation Policy in section 200.4, which applies to designated scenic river segments, states "no degradation shall be allowed in waters which constitute an outstanding resource or have exceptional recreational value and/or ecological significance."

The listed beneficial use as aesthetics does have a stipulation regarding nutrients. It states, "nutrients from point source discharges or other sources shall not cause excessive growth of periphyton, phytoplankton, or aquatic macrophyte communities which impairs any existing or designated beneficial use." These same scenic river segments are also classified as "Outstanding Resource Waters" and as such, non-point source discharges are to be controlled using best management practices in the watersheds.

9

Illinois River Basin

The headwaters of the Illinois River are in the Boston Mountains of northwestern Arkansas in Washington County, about 24 kilometers southwest of Fayetteville. The stream flows in a northerly and westerly direction through this Ozark region, crossing the Oklahoma/Arkansas state line near Siloam Springs, Arkansas. The river continues in a westerly direction until it is joined by Flint Creek. It then flows in a southerly direction to its confluence with the Arkansas River in Sequoyah County near Gore, Oklahoma. The river flows approximately 260 kilometers from its headwaters to its confluence with the Arkansas River (Figure 1).

Two of the major tributaries of the Illinois River also have their origins in the Ozark region of Arkansas. Flint Creek, originating in Benton County, Arkansas, flows in a westerly direction out of Arkansas through Delaware County, Oklahoma and joins the Illinois River from the north just south of Kansas, Oklahoma. Baron Fork Creek originates in Washington County, Arkansas and flows in a southwesterly direction to its confluence with the Illinois River just south of Tahlequah, Oklahoma. Both of these tributary basins are largely forested. Osage Creek, a smaller tributary of the Illinois River, flows southwesterly from Rogers, Arkansas to its confluence with the Illinois River about 16 kilometers east of Siloam Springs, Arkansas. Sager Creek is a tributary of Flint Creek that originates just east of Siloam Springs, Arkansas and flows northwesterly joining Flint Creek in Delaware County, Oklahoma about five kilometers west of the Oklahoma/Arkansas state line.
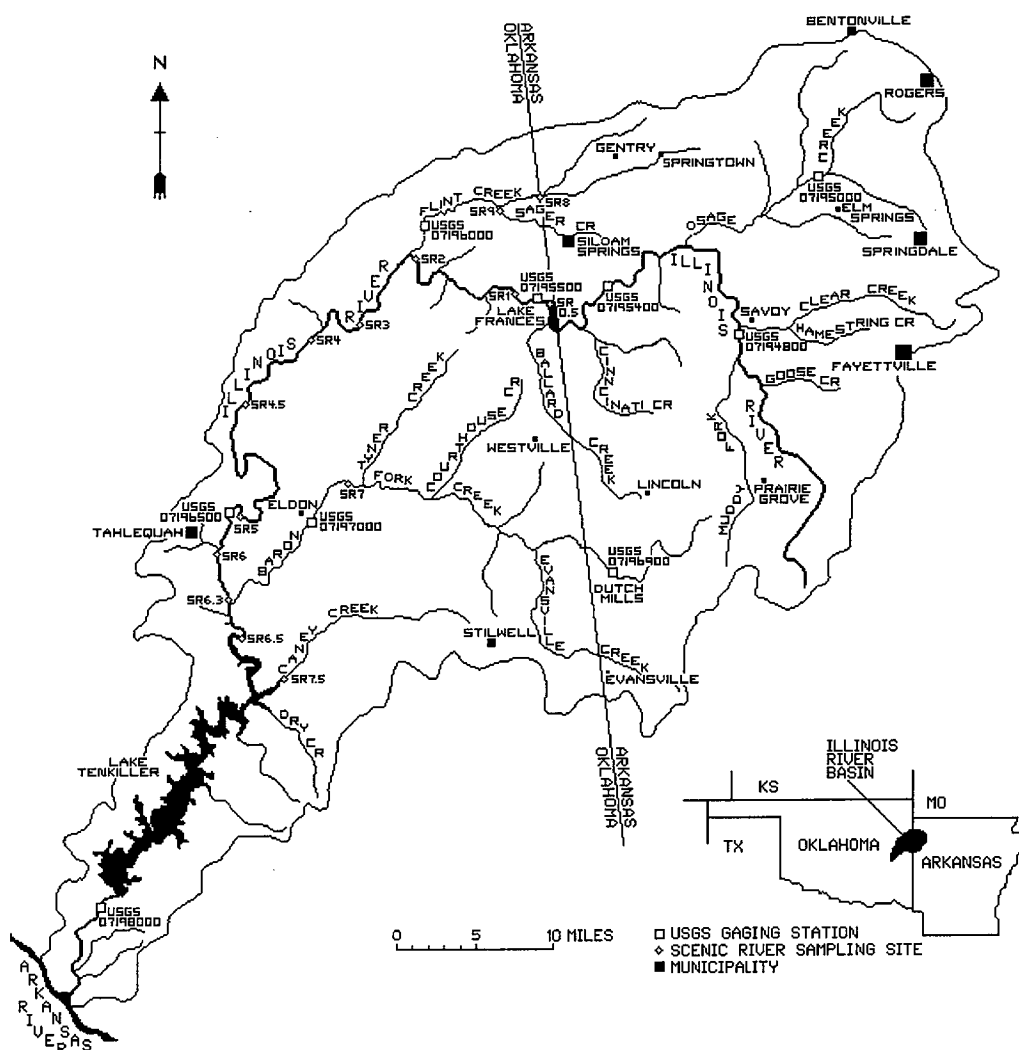
Figure 1.   A Location Map of the Illinois River Basin in Oklahoma and Arkansas Indicating Locations of Water Quality Monitoring Stations, Municipalities, the Illinois River and its Major Tributaries.

The Illinois River Basin, including about 4,300 square kilometers, lies within the southwestern portions of the physiographic province called the Ozark Uplift that covers nearly 103,600 square kilometers in Missouri, Arkansas, and Oklahoma. Approximately 53% of the Illinois River Basin is in Oklahoma while the remaining 47% is in Arkansas (Lyhane, 1987). The Illinois River and its

11

tributaries are included in a part of the Ozark Uplift called the Springfield Plateau.

This plateau is generally deeply dissected with rolling upland areas separated by

V-shaped stream valleys that range from 60 to 90 meters in depth. Geologic

processes have created cliffs of erosion resistant rock along much of the Illinois

River and to a lesser extent on the Flint Creek and Baron Fork Creek basins

(U.S. Dept. of Interior, 1979).

Soil types in the basin range from soils derived from sandstones, shale,

clay, and some limestones.   These soils support vegetation ranging from tall

grasses to oak, hickory and pine forests (Lyhane, 1987). Estimated land use

percentages calculated by the U.S. Dept. of Agriculture - Soil Conservation

Service of Arkansas and Oklahoma (USDA-SCS AR/OK) in a 1989 report show

that about 42% of the basin is forested, 48% is grassland, 3% is urban, 2% is

cropland, and the remaining 5% is a mixture of water, feedlots, and other minor

land use types.

Georeferenced land uses in the Illinois River Basin were obtained from

the U.S. Environmental Protection Agency (U.S. EPA). Maps were derived from

photo interpretation of 1:24,000 scale color infrared aerial film positives flown

from August 30 - September 1, 1985. This information was transferred to clear

mylar overlays based on USGS 7.5 minute (1:24,000 scale) quadrangles.

Digitization and polygon attribution was performed based on these mylar

overlays. Land uses derived from this information were reclassed into seven

broad categories for use in the SIMPLE model. Table I shows the land use/land

cover statistics for the Illinois River Basin above the Lake Tenkiller Dam based

12

on these 1985 data. The results are very similar to Lyhane (1987) with 49% of the basin classified as Pasture/Range and nearly 44% Forest.

TABLE I

LAND USE TYPES AND AREAS FOR THE ILLINOIS RIVER BASIN
IN OKLAHOMA AND ARKANSAS BASED ON 1985 DATA

Land Use Description	Oklahoma Portion Area (ha)	Oklahoma Portion Area (%)	Arkansas Portion Area (ha)	Arkansas Portion Area (%)	Illinois River Basin Area (ha)	Illinois River Basin Area (%)
crop	880	0.4	3,890	2.0	4,770	1.2
confined animals	224	0.1	1,400	0.7	1,620	0.4
forest	121,000	56.2	56,900	29.5	178,000	43.6
pasture /range	84,100	38.9	118,000	61.2	202,000	49.4
roads & ROW	478	0.2	654	0.3	1,130	0.3
urban	2,850	1.3	11,500	6.0	14,400	3.5
water	6,090	2.8	649	0.3	6,740	1.7
totals	216,000	100	193,000	100	409,000	100

The significant economic benefits of recreation on the Illinois River can be explained in part by the extensive use of the Illinois River by canoeists. The Oklahoma Scenic Rivers Commission has tallied the $1.00 per canoe user fee paid at the numerous canoe rental operations on the river. Results show 52,000 to 67,000 canoes were rented each year from 1984 to 1988 (USDA-SCS AR/OK, 1989). Lake Tenkiller is also a popular recreation area with more than 1.5 million visitors each year from 1992 to 1994 (OWRB, 1996).

13

Lake Frances

Lake Frances, one of two impoundments on the mainstem of the Illinois River, a 570 surface acre lake located in Adair County in Oklahoma and Benton County, Arkansas, was first impounded in 1931. In 1954, the City of Siloam Springs, Arkansas purchased the dam and most of the adjacent land with the intentions to rebuild the dam and use the reservoir as a water supply source. The dam is considered the upper limit of the scenic river portion of the Illinois River.

Water supply is the major commercial use of Lake Frances. It serves as a water supply source for Siloam Springs and other small communities in the area both in Arkansas and Oklahoma. The lake provides some recreational uses as a fishery but the lake is generally too shallow to be used for recreational boating other than fishing.

Concerns have been raised about the dam impounding Lake Frances. The U. S. Army Corps of Engineers and the Oklahoma Water Resources Board have declared the dam a safety hazard. The Oklahoma Water Resources Board has ordered the City of Siloam Springs to repair the aging dam. The City of Siloam Springs has since offered to sell the dam and the lake for a nominal fee. There are currently alternatives being discussed which include removing the dam and draining the lake, or repairing the dam and dredging the lake. Part of the top of the dam broke off during flooding in May 1990.

Lake Frances is relatively shallow with a mean depth of 1.2 meters. The lake has a short hydraulic retention time of about two days (Threlkeld, 1983).

14

The lake suffers substantial seasonal algal blooms that deter from its attractiveness as a recreational area. These blooms have been cited as a possible cause for decreased water quality in the Illinois River several kilometers below the dam (Burks et al., 1991).

Lake Tenkiller

The Lake Tenkiller dam is on the Illinois River about 11 kilometers northeast of Gore, Oklahoma. The lake extends more than 40 kilometers up the Illinois River in Cherokee and Sequoyah counties and at normal power pool of 632 feet mean sea level has a surface area of approximately 12,900 acres, 209 kilometers of shoreline, and a volume of 654,100 acre-feet (U. S. Army Corps of Engineers, 1988). The lake was completed by the U.S. Army Corps of Engineers in 1952 with authorized project purposes being flood control and hydro-power generation. The lake also serves as a water supply source for numerous municipalities in the immediate vicinity and is valued as a prime recreational facility (Nolen et al., 1988). The lake is primarily fed by the Illinois River with the main tributaries being Flint Creek, Baron Fork Creek, and Caney Creek which enters the lake directly.

Several studies have been performed on the lake to estimate its current and future trophic status because concerns have been raised about water quality deterioration in the Illinois River Basin. Because flow velocities along the mainstem of the Illinois River are relatively high even during low flow periods, and because Lake Frances has a low mean hydraulic retention time, nutrient

15

discharges from the upper Illinois River watershed are likely to end up in Lake

Tenkiller (Walker, 1987a).

CHAPTER III

LITERATURE REVIEW

Illinois River Basin Water Quality Studies

Several water quality studies have been performed on various segments of the Illinois River Basin over the past 15 years. The Oklahoma State Department of Health (1977) conducted studies in the Illinois River Basin from June 1975 to October 1977 that included assessments of Lake Frances and Lake Tenkiller, the Illinois River from Lake Frances to Lake Tenkiller, and portions of Flint Creek and Baron Fork Creek. Lake Frances was described as being in the late stages of eutrophication. The impact of the outflow from Lake Frances was determined to extend downstream to the Illinois River's confluence with Flint Creek. Flint Creek was shown to be carrying elevated loads of nutrients. Baron Fork Creek was judged to have superior water quality. Water quality in the Illinois River generally improved going downstream from Lake Frances to Lake Tenkiller. Lake Tenkiller was described as having high water quality and was classified as mesotrophic.

Threlkeld (1983) conducted a diagnostic feasibility study for the potential restoration of Lake Frances from October 1981 to October 1982. The study

included regular sampling of sites in Lake Frances, inflows from the Illinois River

and Ballard Creek, and the outflow from Lake Frances. The lake was described

as very eutrophic and the primary cause was attributed to phosphorus entering

the system from discharges from Springdale and Rogers' wastewater treatment

plants (WWTPs). It was concluded that Lake Frances was heavily loaded with

both nitrogen and phosphorus but that the lake retained negligible amounts of

these nutrients partially due to the short hydraulic retention time of about 2.4

days.

Threlkeld (1983) concluded that dredging of the upper end of Lake

Frances was necessary to increase the residence time of waters in the lake to

allow for greater retention of nutrients by the lake. Also, the treatment of

phosphorus in the WWTPs at Springdale and Rogers would greatly reduce

phosphorus entering the lake. Nutrient loading from the Lake Frances

watershed was determined to contribute to water quality degradation in the

Illinois River downstream of Lake Frances.

The U.S. Geological Survey (Terry et al., 1984) conducted an extensive

water quality study on the Illinois River Basin above Lake Frances from

September 1978 to September 1981. The purposes of that study were to

determine existing water quality conditions and to calibrate and verify an in-

stream water quality model that would be used to simulate changes in water

quality caused by changes in nutrient loadings. The study concluded that

existing water quality in the Illinois River, and several major tributaries, did not

meet the Arkansas State Guideline of 100 µg/l total phosphorus (as P) in

streams.

Roberts/Schornick and Associates (1984) reviewed studies of the Illinois River Basin for the Office of the Attorney General of Oklahoma in response to the City of Fayetteville's plan to upgrade their existing wastewater treatment plant and divert part of the effluent into a sub-tributary of the Illinois River. They concluded that the quality of water in the Illinois River apparently improved going downstream from Lake Frances, but indicated that the river was probably assimilating as much waste as possible and that increased loads of nutrients would generate increasing water quality problems.

Oklahoma's 305(b) Report (Oklahoma Department of Pollution Control, 1984) included an assessment of trends for certain water quality parameters at USGS gaging stations 07195500, 07196000, 07196500, and 07197000 for the period from 1975 to 1983 done by the Oklahoma Department of Pollution Control (ODPC). It was concluded there was an apparent increasing trend in concentrations of total phosphorus at all four stations. Nitrite + nitrate (NO_2+NO_3) trend tests showed no apparent trend at USGS stations 07195500 and 07197000. USGS 07196000 showed an apparent decreasing trend and 07196500 showed a possible decreasing trend. The ODPC used a U.S. EPA software package that applied Spearman's Rho and Sen test statistics to analyze the data. These are nonparametric tests for trend based on rank correlated with time. In the report, an 'apparent' trend was defined as being statistically significant at the 90% level, and a 'possible' trend was defined as being statistically significant at the 80 - 90% level.

Gakstatter and Katko (1986) performed an intensive study of the Illinois River Basin in both Arkansas and Oklahoma in August 1985. This study was done in response to concerns that water clarity had decreased in the reach of the Illinois River between Lake Frances and Lake Tenkiller, the designated scenic river portion. The survey included water sample collection and analysis of 24 mainstem and tributary sites throughout the basin. The study concluded that background phosphorus concentrations in the basin were generally very low. However, Osage Creek, which receives wastewater effluent from the cities of Rogers and Springdale, Arkansas, typically had much higher phosphorus concentration levels that substantially affected concentration levels in the Illinois River above Lake Frances and in Lake Frances. It was also concluded that the effects of water flowing through Lake Frances, sustaining substantial algal growth, adversely affected water clarity for some 32 kilometers below the Lake Frances dam.

Walker (1987a) prepared a report for the Office of the Attorney General of Oklahoma in response to the proposed discharge of a portion of Fayetteville's effluent into the Illinois River Basin. Reviewing data in the EPA's STORET data base and Gakstatter and Katko's data, Walker concluded that phosphorus concentrations have increased by a factor of roughly two to three over the past decade. The increased levels of stream phosphorus have been accompanied by substantial increases in chlorophyll *a* concentrations in both Lake Frances and Lake Tenkiller. Chlorophyll *a* is a pigment produced by algae and is an indicator of algal density. Walker used flow-weighted annual mean total phosphorus

20

concentrations to develop conclusions about trends. He suggested that it would only be proper to compare years of comparable flow to determine if total phosphorus concentrations had indeed increased. Walker also concluded the most probable cause for accelerated eutrophication in Lake Tenkiller is increased point source nutrient loadings. Generally, nonpoint sources tend to be rich in nitrogen while point sources tend to be rich in phosphorus (Walker, 1987a).

A study done by the U. S. Army Corps of Engineers (1988) on Lake Tenkiller in 1985 and 1986 showed relatively high concentrations of nutrients in the upper portion of the lake which gradually decreased going downstream toward the dam. Using a trophic state index proposed by Carlson (1977), which provides a numeric measure of trophic status using total phosphorus data, the lake was classified as eutrophic throughout the lake. Carlson's index can also use chlorophyll *a* and secchi disk data to determine trophic status. Using these data the lake was shown to be borderline eutrophic at the upper end decreasing to mesotrophic near the dam. It was concluded "immediate and intense" efforts by federal and state agencies, municipalities, industries, and private landowners would be required to control point and non-point sources of nutrients to protect Lake Tenkiller from further deterioration.

Burks and Kimball (1988) performed a study evaluating existing concentrations of nutrients transported by the Illinois River to make an assessment of the potential effects on water quality in Lake Tenkiller. They found the highest levels of nutrient concentrations (nitrogen and phosphorus)

just below Lake Frances with a steady decline downstream to Tahlequah where

that city's WWTP effluent caused an apparent increase. A steady state

computer model, QUAL2E, of the lower reaches of the Illinois River above Lake

Tenkiller and the upper segment of Lake Tenkiller was developed. They found

that a projected decrease in phosphorus concentration input from Tahlequah's

WWTP, after construction and implementation of a phosphorus removal system,

would be adequate in reducing the rate of eutrophication of Lake Tenkiller.

However, they concluded that other point and non-point sources within the basin

would still contribute to the further deterioration of water quality in Lake Tenkiller.

They recommended concerted efforts by public and private agencies to reduce

phosphorus input into Lake Tenkiller to prevent further deterioration.

Harton (1989) performed a modeling study of the Illinois River in an

attempt to analyze contributions of point and nonpoint source phosphorus

loading on Lake Tenkiller. Included in the objectives of the study was an attempt

to determine the effects of the discharge of half of Fayetteville, Arkansas' treated

effluent into a tributary of the Illinois River and the subsequent effects on

eutrophication in Lake Tenkiller. The Fayetteville wastewater treatment plant

effluent was determined to have no observable effect on eutrophication in Lake

Tenkiller. Harton concluded that the substantial distance from the point of entry

of the effluent into the Illinois River to Lake Tenkiller was sufficient to allow for

nearly total removal due to sedimentation and biological activity. Non-point

source total phosphorus loadings from Oklahoma and Arkansas were found to

be the main loading sources to the lake. Harton concluded that removal of 70 to

22

90% of the total phosphorus loading from point and nonpoint sources would be necessary to bring eutrophication under control at Lake Tenkiller.

A study by Burks et al. (1991) attempted to evaluate factors affecting water quality in the Illinois River. It was found that in-stream total phosphorus concentration exceeded the 0.1 mg/l level recommended by the EPA (U. S. EPA, 1986) to prevent enrichment of streams or tributaries to standing bodies of water. They suggested that there was "overwhelming evidence" that phosphorus loading to the upper end of Lake Tenkiller was excessive, and predicted decreases in water quality for the lake. Total nitrogen loading also was shown to be increasing over time. They suggested strict reduction of both point and nonpoint nutrient inputs into the system, and suggested that the focus be placed on phosphorus.

The Phase I Diagnostic and Feasibility Study on Tenkiller Lake (OWRB, 1996) found that mean annual concentrations of phosphorus, nitrogen, and chlorophyll *a* measured throughout Lake Tenkiller were indicative of eutrophic conditions. The entire lake was found to be affected by eutrophication as evidenced by the presence of anoxic conditions in the hypolimnion during summer stratification. Recommendations for control of eutrophication were focused on the reduction of phosphorus from both point and nonpoint sources.

Evidence suggests that there have been upward trends in the levels of nitrogen and phosphorus at water quality monitoring stations within these scenic river segments. Gade (1990) presented temporal trend tests (Kendall Tau) on flow adjusted concentrations of total phosphorus at USGS gaging stations

07195500 (Illinois River at Watts, OK), 07196000 (Flint Creek near Kansas, OK), 07196500 (Illinois River near Tahlequah, OK), and 07197000 (Baron Fork Creek near Eldon, OK) all indicated highly significant upward trends for the period from 1976 to 1986. Flow adjusted concentrations of nitrogen, measured as NO_2+NO_3, showed highly significant increasing trends at 07195500 near Watts and at 07194800 (Illinois River near Savoy, AR, not a scenic river segment) using the Kendall Tau test over the same time period.

Phosphorus

From a biological standpoint, phosphorus is necessary in small quantities for the proper nutrition of plants, animals, and man. The reproductive processes of life depend on the phosphorus-containing genetic code carriers DNA and RNA. Life cannot proceed without the energy exchanges mediated by vital phosphates such as ATP (Toy and Walsh, 1987). No other element in fresh waters has been studied as intensively as phosphorus. Ecological interest in phosphorus stems from its major role in biological metabolism, and the relatively small amounts of it available in the hydrosphere. It is the least abundant of the major structural and nutritional components of biota (carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus) and most often limits biological productivity in aquatic environments (Wetzel, 1983).

In aquatic ecosystems, as in all ecosystems, specific amounts of nutrients and trace elements must be available to living organisms in order for them to survive and proliferate. In many freshwater aquatic ecosystems, phosphorus as

24

phosphate is often referred to as a "limiting nutrient" implying that it is normally

not abundantly available in forms usable by organisms. If the amount of

phosphate available to organisms is very small, then the growth of organisms is

limited by that low availability. If the amount of phosphate is abundant or in

excess of the amounts required for life maintenance of organisms, then the

organisms will tend to proliferate until another of the essential nutrients or

elements becomes limiting, or until the organisms begin to alter their

environment in such a way that is detrimental to themselves or other life forms.

Concerning freshwater ecosystems, excessive input of phosphate tends

to accelerate the natural aging process of lakes and streams (eutrophication).

Eutrophication, as a natural geological process, involves a body of water where

organic life develops and multiplies through time. Organisms flourish and die in

normal life cycles and, with time, the bottom surface of the water body

accumulates the remnants of organic life and inorganic sediments, and slowly

builds up. As the water body becomes shallower, the aquatic organisms change

character. Eventually the water body becomes so shallow that it becomes a

marsh, bog, or swamp. Finally, the water body no longer exists as such, and

becomes dry land. This process normally takes thousands of years for a

relatively large body of water (Toy and Walsh, 1987).

Our present concern is that with the inflow of excessive quantities of

nutrients into water bodies, caused by the activities of man, eutrophication is

rapidly accelerated. An example is Lake Erie's shallow western basin. It has

been estimated that in the past 50 years this area of the lake has aged an

equivalent of 15,000 years (Toy and Walsh, 1987).

Phosphorus is the eleventh most abundant element in igneous materials in the earth's crust. Average concentration of phosphorus in this environment is estimated as about 1% by weight and thus it is classified as a trace element. Only a fraction of this amount is concentrated in deposits consisting mainly of phosphate minerals (Holtan et al., 1988). Pure phosphorus is a white, transparent, crystalline, waxy solid that glows in the dark and ignites in air just above room temperature (30 $^{\circ}$C) and melts at 44.2 $^{\circ}$C (Toy and Walsh, 1987).

Phosphorus in the environment occurs almost exclusive as phosphate in the +5 oxidation state. Phosphine (PH_3) appears to be absent from biochemical and geochemical systems. In its general chemistry, phosphorus has a strong affinity for oxygen (Corbridge, 1985). Orthophosphate (H_3PO_4), the form of phosphorus found in natural environments, has a melting point of 42.35 $^{\circ}$C, a boiling point of 213 $^{\circ}$C, solubility of 1.0×10^6 at 25 $^{\circ}$C, specific gravity of 1.834, and vapor pressure of 0.0285 mm Hg at 20 $^{\circ}$C. It is a strong acid and therefore in adequate concentration is corrosive (U.S. EPA, 1984). The acid dissociates in three distinct stages in water with dissociation constants of $k_1 = 7.1 \times 10^{-3}$, $k_2 = 7.99 \times 10^{-8}$, and $k_3 = 4.8 \times 10^{-13}$. It is soluble in water and alcohol, and has a molecular weight of 98.00 (Budavari, 1989).

The most significant form of inorganic phosphorus in natural waters is orthophosphate (PO_4^{-3}). A large proportion of phosphate in freshwater occurs as organic phosphate and cellular constituents in biota adsorbed to inorganic and dead particulate organic matter. Total inorganic and organic phosphorus are

26

frequently separated by chemical analyses but these fractions often poorly relate

to the metabolism of phosphorus. Commonly, the most important measure is

total phosphorus of unfiltered water which consists of phosphate in the

particulate and dissolved phases. Particulate phosphate is phosphate in

organisms such as nucleic acids and phosphoproteins (not involved in the rapid

cycling of phosphate), low molecular weight esters of enzymes, vitamins, and

nucleotide phosphates, mineral phases of rocks and soil in which phosphate is

absorbed onto inorganic complexes such as clays, carbonates, and ferric

hydroxides, and phosphate absorbed onto dead particulate matter. Dissolved

phosphate is defined as orthophosphate, polyphosphate (as in synthetic

detergents), organic colloids or phosphate combined with absorptive colloids,

and low molecular weight phosphate esters (Brock, 1985).

Much emphasis on analytic evaluation results in the recognition of eight

different forms of phosphorus with four operational categories. The four

operational categories are soluble reactive phosphorus, soluble unreactive

phosphorus, particulate reactive phosphorus, and particulate unreactive

phosphorus. These operational categories do not necessarily correspond with

chemical species of phosphorus or to their role in the biotic cycling of

phosphorus.

Separation of total phosphorus into inorganic and organic fractions in a

large number of lakes indicates that a large majority of the total phosphorus is in

an organic phase (usually around 90%). About 70% of the organic phosphorus

is found within particulate organic material and the remainder found as dissolved

or colloidal organic phosphorus. Inorganic phosphorus is consistently present in very low concentrations and is cycled very rapidly in the zone of utilization. The ratio of inorganic phosphorus to other forms is approximately 1:20 or about 5%. The percentage as orthophosphate is then less than 5% (Wetzel, 1983).

Phosphate is present in lakes at only one oxidation state (PO_3^-), so that complications regarding oxidation and reduction do not arise. Soluble phosphorus is that fraction assayable by orthophosphate assay after filtration of a water sample through a membrane filter (pore size generally 0.45 µm). Total phosphorus is that assayable after digestion of an unfiltered sample with a strong oxidizing agent (perchlorate or persulfate) followed by an orthophosphate assay. Insoluble phosphorus is the difference between total phosphorus and soluble phosphorus. The soluble form is almost certainly available to phytoplankton, whereas the particulate form may or may not be available (Brock, 1985).

Phosphate deposits may be classified into three broad apatite [($Ca_5(PO_4,CO_3)_3(F,Cl,OH)$)] groups which are apatite deposits of igneous and metamorphic origin, sedimentary phosphorites, and guano and related deposits. More than 200 natural phosphates have been described. Most (95%) occur as fluorapatite (Holtan et al., 1988).

Calcium phosphate from animal bones was used as a source of inorganic phosphorus in the past. Present sources of calcium phosphate are minerals commonly known as phosphorite or phosphate rocks mined in enormous open pits. The phosphate rocks have an approximate composition of the mineral

28

fluorapatite $Ca_5(PO_4)_3F$, a calcium phosphate containing 4% fluorine. Largest American deposits of phosphate rocks lie in Florida, Tennessee, North and South Carolina, Kentucky, Virginia, Utah, Idaho, and Montana. Florida is largest producer of phosphate rock which is a five billion dollar a year business. Large deposits are also found in Kola Peninsula in Scandinavia, Algeria, Tunisia, Egypt, and Morocco (Holtan et al., 1988). In 1980, approximately 37 million tons of phosphate rock was consumed in the U.S.. About 7% of this was used to produce elemental phosphorus and the remainder was converted to phosphoric acid and fertilizer products. In 1984 the U.S. produced more than 750 million pounds of the element (Toy and Walsh, 1987).

Origin of these rocks is believed to be the small quantities of phosphate normally present in granitic rocks. Over eons of time, through weathering and leaching, phosphates found their way into the sea where marine animals absorbed and concentrated them into their shells, bones, and tissues. The remains of these animals accumulated on the bottom of the sea and over the years, through geological changes, some phosphatic sediments appeared as deposits on dry land (Altschuler, 1973).

The release and export of phosphate from uncultivated soil is a function of the geology and soil composition, air temperature, precipitation, and hydrological conditions. Generally, waters in contact with unfertilized soils give a range of phosphorus concentrations less than 0.01 mg/l. Areas dominated by sedimentary rock systems tend to contribute more phosphorus to runoff than areas dominated by igneous rock formations (Holtan et al., 1988).

A major fraction of the total phosphate carried out of a watershed by streams is associated with the particulate matter suspended in the water, much of which is delivered during a relatively short period of time when discharge rate is high and the velocity of the flowing waters is sufficient to transport particles of varying sizes and densities. A smaller fraction is dissolved in the water.

An adult human normally excretes 1.3 - 1.5 grams of phosphorus per day and disposes of an additional quantity through the use of synthetic detergents. Phosphate detergents have become one target in the attempt to reduce phosphorus release into the environment. Phosphorus removal from sewage by municipal waste water treatment plants has become a standard process in some regions (Holtan et al., 1988).

Another major source of phosphorus is agricultural activity, either derived from crop production (fertilizers) or from animal wastes. Application of fertilizers to agricultural land to increase productivity has resulted in the off-site transport of some of the nutrients through leaching and runoff. The recent trend to produce livestock in larger farm units has, in some areas, led to high concentrations of livestock wastes washing into streams and lakes (Holtan et al., 1988).

After use by man, a significant fraction of phosphorus is transported to watercourses in particulate and dissolved forms by means of agricultural runoff or as point sources from municipal waste water treatment plants. Ground water discharge and atmospheric deposition also contribute to phosphate loading of streams and lakes (Holtan et al., 1988). There is great regional variation in phosphate concentration in precipitation. This can be a major source in some

lakes. Phosphorus sources which accelerate eutrophication are often anthropogenic and include point sources of treated wastewater effluent and nonpoint sources associated with agricultural activities.

The movement of phosphate through the inorganic and organic forms can be resolved into three main cycles. This is, in essence, two biological cycles superimposed on an inorganic cycle. The inorganic cycle turns very slowly with its rate of revolution measured in 10^9 years. The two biocycles turn rapidly in comparison. The land-based biocycle may have an annual turnover of some of the phosphate, although there are reservoirs of phosphate in the soil that can store it for centuries. In the water-based biocycle phosphate turnover is often measured in days and months.

The primary inorganic phosphate cycle is probably better described in terms of a spiral rather than a cycle. Phosphate originally comes from igneous rocks and, via weathering and biological processes, passes through the soil to the rivers and on to the sea, where it eventually ends up in sediment. If the sediment is part of the deep ocean there is little chance of that phosphate going through the cycle again. However, some ocean phosphate does return to land via ocean currents, fish, and the birds that feed on them. If the sediment is part of an inland sea or continental shelf there is a good chance it will once again be part of dry land as a result of geological uplift. The overall natural movements tend to concentrate phosphates in large deposits in a few areas of the globe, chiefly along the western coasts of the continents. The spiral would tend to end there except for the intervention of man who can release this locked-up

31

phosphate to the inorganic cycle again (Emsley, 1980).

The atmosphere does not serve as a significant reservoir of phosphate, but its contribution to the phosphates found in water bodies through wet and dry deposition is significant. The development of phosphorus budgets for water bodies are necessarily required to account for atmospheric deposition of phosphorus on lake and stream surfaces. The importance of atmospheric sources of phosphorus increases when the land area/lake area ratio increases. In some very dilute lakes of Western Ontario, precipitation may account for as much as 80% of the phosphorus input (Ahl, 1988).

Phosphorus exists in the atmosphere in dust particles and microbial debris. That means that all phosphorus collected as wet or dry deposition has earth as its origin (Ahl, 1988). Atmospheric dust originates from three major sources which are terrestrial airborne matter, volcanic, and cosmic. Of these, the terrestrial dust makes up the main bulk. Deserts and other dry regions act as major sources of atmospheric phosphorus and the soil composition of a wind eroded area can be reflected 200 - 250 km away (Ahl, 1988). Anthropogenic contamination of the atmosphere includes phosphorus coming from fertilized soils.

Differentiation of terrestrial and marine atmospheric phosphorus contributions can be made on the basis of the relative quantities of reference elements (Si, Na and Cl for marine, and Al and Fe for terrestrial) in the atmospheric dust particles. Generally, air masses with oceanic origin have much lower content of phosphorus than air masses with continental origin. Ahl (1988)

32

described a study of coastal aerosols in a low industrial area in Brittany, France at the Atlantic coast and found that air masses of continental origin contained phosphorus of crust origin up to 40%. The anthropogenic phosphorus content, independent of origin, varied from about 60 to 90% of the total amount.

Most of the terrestrial dust carries phosphorus in the inorganic form. A U.S. average estimate of background atmospheric deposition is in the range of 10-46 kg phosphorus $km^{-2}yr^{-1}$. Lowest deposition figures indicate that lowest phosphorus deposition in the Northern Hemisphere is found in remote areas (Ahl, 1988).

Soil formation (pedogenesis) is an ongoing process that is partly mechanical (weathering) and partly a consequence of supporting living things. Pedogenesis slowly releases inorganic phosphate from apatite fractions of the original rocks to the water in the soil, where it becomes available for plant nutrition. This source of phosphate is released too slowly to represent a significant contribution to the phosphate required for a particular growing season. The water in the soil generally has a concentration of 10^{-5} to 10^{-6} M phosphate but may be as low as 10^{-8} M in some tropical soils (Emsley, 1980). It has been observed that the concentration of plant available phosphorus in the top soil remains almost constant when crops are being grown which indicates that there are insoluble sources of phosphate in the soil which supply the soil water with phosphate to maintain an equilibrium concentration.

In addition to the supply of phosphate from the original rocks and rainwater, it is possible to identify three pools of phosphate that can supply it to

the soil water. These can be described as either non-equilibrium pools, such as the original apatite and the organic phosphate, from which the phosphate is slowly released, or equilibrium pools such as the precipitated and adsorbed phosphate pools. These labile pools can release phosphate to soil water or remove phosphate from soil water as conditions permit (Emsley, 1980).

Phosphate has a special relationship with three metals in soils (calcium, iron and aluminum). Calcium phosphate is essentially insoluble but does not remove phosphate permanently and remains in equilibrium with a certain concentration of phosphate in the soil solution. Aluminum hydroxide, on the soil particle surface, is the principle holding agent for inorganic phosphate and acts as a ligand to it in the $H_2PO_4^-$ form. It holds the HPO_4^{-2} ion less securely and for this reason an increase in soil pH will release phosphate bound to aluminum (Altschuler, 1973). Thus, liming soil has the effect of releasing more aluminum bound phosphate than it precipitates as calcium phosphate. Phosphate attached to aluminum is labile and crystals of definite composition may form (Emsley, 1980).

Phosphate attached to iron is immobile and is described as occluded. Ferric hydroxide sites on the soil surface can hold phosphate permanently, and the gradual buildup of occluded phosphate is due to its migration to and retention to these sites. Phosphate attached to iron is not labile nor does it crystallize (Emsley, 1980). During periods of lake stratification, where the hypolimnion can become anoxic, decreased redox potentials can result in the release of phosphate and iron from lake sediments into solution (Wetzel, 1983).

34

Biological interactions with phosphates in the soil and soil solution can be used to describe the land-based biocycle. Roots are good at scavenging phosphate from the soil water and then it begins through a biocycle. The ratio of plants to animals is the determining factor in the rate of phosphate flow through the system. In systems with little animal activity, the uptake of inorganic phosphate from the soil may be as little as half that from systems supporting dense animal activity. Roots can transfer phosphate against a concentration gradient from soil water to plant. By doing so they create in turn a concentration gradient for the precipitated and adsorbed phosphate in the soil, causing them to release phosphate to the soil solution.

The role of soil fauna and microbes is a key part of the phosphate cycle. These decomposers require phosphate for their own metabolic needs and studies have shown that they take up four to five times more soil phosphate than do plants living in the same soil. They also add organic phosphates to the soil. It has been estimated that 75% of organic phosphate in the soil comes from microbial sources (Emsley, 1980).

In general, the loss of phosphate from soils via leaching is relatively small since it is tightly bound to particulate matter. The amount lost by leaching is probably compensated for by phosphate arriving in rainwater.

Phosphate cycling in water bodies via biological means can be described as the water-based biocycle. The routes for conveying phosphate from the land cycle to the water-based cycles are for the most part rivers and streams. It has been estimated that rivers carry 17 million metric tons of phosphorus to the seas

35

each year, half due to natural processes and half due to the activities of man (Emsley, 1980).

Phosphate moves rapidly through the water-based system. The two factors which determine the extent of biomass in most lakes and seas are the availability of phosphate and the amount of solar energy. This cycle again represents a downward spiral as the processes of precipitation and sedimentation are responsible for the rapid loss of phosphate from the aqueous phase to the solid phase at the bottom.

Phosphate uptake in the aquatic system into biomass is very rapid. Algae, like land plants, can take in more phosphate than they actually need and can store enough surplus to support them through about three cell divisions without additional input (Emsley, 1980). Algae are able to directly utilize the inorganic phosphate and given the combination of a plentiful supply and enough sunlight they can multiply to such an extent as to color the water green or red in lakes. Often two blooms of algae appear each year. In Spring the sunlight and mixing waters rich in phosphate will often promote a bloom. In Fall, phosphate mixed upward from the deeper layers of the lake becomes available to the algae once again and a second bloom may appear. Phosphate in algae can be taken up and released rapidly. Within hours of death, the cellular phosphate is released into the water again as either inorganic phosphate or soluble organic phosphate which can be readily taken up by living algal cells (Emsley, 1980).

It has been observed that relatively low concentrations of phosphate in waters could support algal blooms, which seems at odds with the idea of

36

phosphate as a limiting nutrient. But, it is not the concentration of inorganic phosphate which is most important, but rather the total phosphorus concentration, since rapid recycling occurs.

The lake sediment is often the final resting place for phosphate. It may remain here for millions of years. Phosphate in the top layer of sediment can, however, return to the waters of a lake by various means. Decomposer organisms, enzymes, worms and other benthic organisms may assist this process. Certain forms of organic phosphate can form stable complexes with metals and this phosphate is not released.

When the waters of a lake become stratified the lowest layer may become anoxic due to oxygen depletion as a result of the degradation of organic debris settling down from the upper layers. The hypolimnion may also become slightly acidic. Both of these conditions, a reducing and an acidic solution, will facilitate the return of phosphate from the upper layer of the sediment back into solution. Phosphate held in the sediment as insoluble $FePO_4$ will be reduced to soluble $Fe_3(PO_4)_2$ and insoluble $CaHPO_4$ will be acidified to soluble $Ca(H_2PO_4)_2$. Under these conditions the release of phosphate from the sediment can sometimes exceed the downward flow of phosphate to it. The top layer of sediment in a eutrophic lake may hold enough phosphate to keep the lake in a eutrophic state despite effective steps taken to curb the inflow of phosphate into the lake (Emsley, 1980).

Sediments play an important role in the overall phosphorus metabolism of lakes acting as both a source and a sink. In most lakes there is a net deposit of

37

phosphorus in the sediments. However, in lakes of higher trophic status,

phosphorus release may exceed phosphorus sedimentation for periods ranging

from days to a year. Oxygenated sediments tend to retain phosphorus by

fixation to iron (III) while reduced sediments release phosphorus by reduction of

iron and subsequent dissolution of iron-phosphorus complexes (Bostrom et al.,

1988). Lake sediments generally contain much higher concentrations of

phosphorus than the overlying water. Under aerobic conditions the exchange

equilibria is directed largely toward the sediment. Under anaerobic conditions,

inorganic exchange at the sediment-water interface is strongly influenced by

redox conditions.

Phosphorus mobilizing bacteria of the genera *Pseudomonas*, *Bacterium*,

and *Chromobacterium* are important in mobilizing phosphorus into the interstitial

waters of the sediments, but bacterial metabolism at the interface has relatively

little effect on the on biogenic fixation and removal of phosphorus from overlying

waters. Under aerobic conditions bacteria at the interface increase transport of

phosphorus to the sediments due to sedimentation (Wetzel, 1983).

In very productive lakes, with high rates of sedimentation of organic

matter to the sediments, the decomposition of the sedimenting organic matter

produces anoxic conditions, hydrogen sulfide, and ferrous sulfide (FeS) is

precipitated. FeS is exceedingly insoluble and forms at a redox potential of

about +100 mv. If large quantities of FeS precipitate, sufficient iron can be

removed to permit some of the phosphate accumulated in the hypolimnion to

remain in solution which can then become available to algal organisms when the

water body mixes (Wetzel, 1983).

Only part of the total phosphorus load to lakes will be available to the lake biota for production of organic matter. Basically, bioavailable phosphate can be defined as the sum of immediately available phosphate, and, phosphate that can be transformed into an available form by naturally occurring physical (desorption), chemical (dissolution), and biological processes (enzymatic degradation) (Bostrom et al., 1988). Orthophosphate seems to be the only directly available phosphorus source for planktonic algae and bacteria although the direct uptake of some organic phosphates cannot be excluded.

Schaffner and Oglesby (1978) defined biologically available phosphate as soluble reactive phosphate (SRP), soluble unreactive phosphate (SUP), and labile phosphate (associated with soil particles). SRP is considered to be entirely biologically available, SUP is considered to be available by enzymatic hydrolysis, and labile phosphate may be available as it dissolves in an aqueous solution.

Bacteria and algae are the only two components of aquatic ecosystems which depend, for their nutrition, on the transport of dissolved substances from the water, through the cell wall/membrane barrier, to the interior of the cell. Utilization of complex organic phosphates has to be preceded by external liberation of orthophosphate by means of enzymes such as phosphatases.

Studies of *E. coli* show that bacterial uptake of phosphate is maintained by two kinetically distinct systems called high affinity and low affinity components. The high affinity system is activated when internal phosphate is

depleted. The low affinity system supplies phosphate at a rate equal to phosphate metabolism within the cell. The high affinity system allows the bacteria to accumulate phosphate against a concentration gradient at a rate faster than the phosphate utilized in the cell (Schaffner and Oglesby, 1978). A membrane localized protein binds one molecule of phosphate per protein molecule. During phosphate starvation the concentration of this protein is capable of increasing by at least one hundred times. The energy source for these systems has been proposed to be ATP, although a close connection between potassium and phosphate transport has been reported with phosphate transport systems appearing to be dependent on the presence of potassium with phosphate and potassium being taken up simultaneously.

Algae also depend on active transport systems for the accumulation of internal phosphate against a concentration gradient. The physiological details of the algal phosphate uptake system are less well known than those of bacteria. It is commonly observed that phosphate-starved algae take up phosphate faster than non-starved algae and in fact rates of uptake may increase 10-100 times. It appears that this response is controlled by internal inorganic phosphate, particularly polyphosphates. The polyphosphate pool is filled during periods of high phosphate supply and can sustain growth for several generations in the absence of external phosphate sources. Light induced energy as ATP from photophosphorylation and oxidative phosphorylation supplies the energy for the uptake (Jansson, 1988).

The sources of phosphate that can be used by algae are varied. The

primary source is inorganic phosphate but other sources can be of importance.

It has been shown that polyphosphate with chain lengths of up to 53 units will

support growths of *Chorella*. The algae have an adaptive enzyme which

hydrolyzes pyrophosphate bonds releasing phosphate which can be used

directly. *Chorella* has also been shown to be capable of deacylating

phospholipids on their cell surface and absorbing the released phosphate

(O'Kelley, 1973).

The level of phosphate required for optimal growth differs among species

of algae. Investigations of minimal and maximal phosphorus concentration, by

Chu (1943) and Rodhe (1948) in Wetzel (1983), grouped freshwater algae into

categories according to their tolerance ranges at or around 20 µg phosphate as

P per liter. Species whose optimum growth and upper tolerance limit is below 20

µg PO_4-P l^{-1} included *Uroglena* and some of the species of *Chara*. Species

whose optimum growth was below 20 µg PO_4-P l^{-1} but had an upper limit above

that concentration included *Asterionella* and other diatoms. Species whose

optimal growth and upper tolerance limit is above 20 µg PO_4-P l^{-1} included green

algae such as *Scenedesmus*, *Ankistrodesmus*, and many others. In these

studies the phosphorus concentrations of the culture media required for optimal

growth were nearly always higher than those in natural habitats where the algae

were growing. The best explanation for this difference is that the chemical mass

of inorganic phosphate in the water has only a tenuous relationship to growth

kinetics. The factor of greatest importance is the rapidity with which phosphate

is cycled and exchanged between the particulate phosphate and soluble

41

inorganic and organic phases (Wetzel, 1983).

The proper functioning of living cells depends on the action of many phosphorus containing compounds. The most important of these are DNA and RNA. These compounds are located in the cells of all living organisms and carry the genetic code. Another important biochemical is ATP, the universal energy carrier in living things. ATP serves as a major link between energy yielding and energy requiring chemical reactions. When one phosphate group in ATP is hydrolyzed at neutral pH at 25 °C to ADP and inorganic orthophosphate, 7,300 cal/mol of energy is liberated (Wetzel, 1983). This free energy of hydrolysis is used to perform biological work. ATP is not the only phosphorus energy carrier in the biological system. Some compounds have a higher free energy of hydrolysis than ATP. These compounds are used for a vast number of biochemical reactions.

The fundamental event in photosynthesis by green plants is the absorption of light by chlorophyll, which raises some of the electrons in the molecule to higher energy levels. The excited electrons are then transferred to electron-carrying enzymes which use the energy in a variety of ways, including the production of ATP (through photophosphorylation) and NADPH. These two energy carriers provide the energy necessary to convert carbon dioxide to glucose in a complex cycle of enzyme-catalyzed reactions. Biophosphates are important as energy carriers and as products of many of these reactions (Corbridge, 1985).

Phosphates are excreted as orthophosphate and some organic

phosphates in soluble form. Laboratory cultures of various species of algae have shown that more than 20% of the total phosphorus in a system may be excreted in organic soluble forms. This dissolved phosphorus can then be readily assimilated by either the species that produced it or another species (O'Kelley, 1973).

A great amount of attention has, and continues to be, directed to the role of phosphorus in eutrophication and the development of algal blooms. It has become widely accepted that the growth of phytoplankton in many bodies of freshwater tends to be limited by the supply of available phosphate. Thus, the addition of quantities of available phosphate to a system, with adequate quantities of all other essential elements and nutrients present, allows the phytoplankton to multiply.

As discussed above, phosphates play a role in a vast number of biochemical reactions. Phytoplankton, as well as all other living organisms, have a requirement for phosphate which, if met, allows normal life processes to proceed. It seems clear that a relationship exists between phytoplankton biomass and phosphorus. A number of studies have shown relationships between phosphorus-loading, summer phosphorus concentration, spring phosphorus concentration, etc., and chlorophyll. When phosphorus concentrations increase the algal biomass also tends to increase (Wetzel, 1983).

Phosphorus limited phytoplankton can respond to changes in phosphorus concentrations by a change in biomass and/or a change in rate of production. If the phosphorus is used to produce biomass that is quickly eliminated, by high

43

grazing pressure for example, the relationship between phosphorus and biomass would weaken unless grazing pressure is also a function of phosphorus. Phytoplankton in different lakes exhibit different strategies for the allocation of phosphorus for either a fast turnover or a high biomass with little turnover. The available nutrients other than phosphorus, as well as environmental conditions such as light, pH, and temperature, may also change the dynamics of phytoplankton in a way that alters its response to phosphorus (Heyman and Lundgren, 1988).

One of the best indicators of advanced eutrophication is the presence of large blooms of algae. Under proper conditions of adequate nutrients, ideal temperature, and correct pH, the rapid growth of microscopic phytoplankton can easily result in highly turbid water. Depending on the species of algae present, the water may turn "pea-green" or red. These algal cells eventually die and decomposition of this organic matter begins. Significant quantities of the organic matter settle to the lake bottom where decomposition continues. This bacterial decay consumes large quantities of dissolved oxygen, sometimes to such an extent that the normal diffusion of oxygen to water is not enough to replenish the supply. Deeper lakes, in regions where conditions exist such that a lake stratifies, eventually have nearly all dissolved oxygen removed from the hypolimnion where it is not readily replenished due to the stability of the stratification and the lack of diffusion from oxygenated layers. The resulting oxygen depletion in the lake effectively excludes oxygen requiring organisms from areas of the lake (Toy and Walsh, 1987).

44

Numerous definitions of lake eutrophication exist based on a variety of applicable conditions associated with increased productivity. Among limnologists, eutrophication is synonymous with increased growth of biota of lakes, and the rate of increasing productivity is accelerated over that rate which would have occurred in the absence of perturbations to the system. The most conspicuous measurable criterion of accelerated productivity is an increased quantity of carbon assimilated by algae and larger plant biomass per unit area.

Under most lake conditions, the most important nutrient factors causing a shift from a lesser to a more productive system are nitrogen and phosphorus. Typical plant organic matter of aquatic algae and macrophytes contains phosphorus, nitrogen, and carbon in approximately the ratios 1:7:40 per 100 dry weight (Wetzel, 1983). If one of these three elements is limiting and the others are present in excess of physical needs, phosphorus can theoretically generate 500 times its weight in living algae (nitrogen - 71 times, and carbon - 12 times). A comparison of the relative amounts of elements required for algal growth with supplies available in fresh water illustrates the general importance of phosphorus and nitrogen. Average plant tissue requirements for carbon, nitrogen, and phosphorus are 6.5, 0.7 and 0.08% respectively. The average supply of these elements in fresh waters is 0.0012, 0.000023, and 0.000001% respectively. The ratios of plant content to supply available then is 5000, 30,000, and 80,000, respectively (Wetzel, 1983). Variations in conditions of solubility or availability may at times make very abundant elements nearly unobtainable, but generally phosphorus and nitrogen are the first to impose limitations on the system

(Wetzel, 1983).

When phosphorus is added as a pulse to an unproductive system, the usual response is a very rapid increase in algal productivity. The increased productivity is not sustained but decreases rather rapidly to levels prior to the addition. Losses to the colloidal fraction and from sedimentation result in continuous losses from the trophogenic zone. Thus, sustained productivity requires the constant input of nutrients. In order to reduce productivity, algal growth is usually most effectively decreased by the reduction of phosphorus inputs into the system (Wetzel, 1983).

The science of ecology teaches us that all living and non-living things in an ecosystem are interrelated and interdependent. Thus, when a system such as a lake rapidly changes, we would expect to find changes in the distribution and presence of species in that community. In response to eutrophication there are documented changes in the distribution and numbers of individuals and species living in the system.

The response of lakes, reservoirs, and slow moving rivers to the over enrichment by nutrients is an increase in fertility, the consequences of which (reduced transparency, increased organic substances, depletion of dissolved oxygen, possible fish kills) adversely affect the different uses of water such as water supply, fisheries and recreation, and impair aesthetic qualities (Vighi and Chiaudani, 1987). Fish species change from salmonid and coregonid species of stringent low thermal and high oxygen requirements to warm water species that are increasingly tolerant of eutrophic conditions.

46

Benthic organisms are also affected. If lakes become extremely enriched to the point that the population densities of the phytoplankton and epiphytes become so great that they shade out the submersed macrovegetation, and then the habitat diversity of the littoral zone diminishes. With increases in eutrophication, and lengthening of the period of hypolimnetic oxygen reduction and associated chemical changes, the rates of respiratory activity of the adapted benthic animals are reduced. Rates of growth and survival also change. Under severe conditions essentially all aquatic insects are eliminated. Oligochaete annelids may be the only group of benthic fauna able to survive. More eutrophy shifts the percentage composition of the two dominant groups of benthic animals in the profundal zone of lakes, the Chironomidae and the oligochaetes. The former are dominant in oligotrophic conditions and the latter in eutrophic conditions (Wetzel, 1983).

In addition to increased populations of all species of phytoplankton with the influx of limiting nutrients, prolonged eutrophic conditions can lead to a change in the types and quantities of species present. Oligotrophic water bodies tend to be dominated by *Chrysophyceae, Cryptophyceae, Dinophyceae,* and *Bacillariophyceae.* Eutrophic water bodies tend to be dominated by *Bacillariophyceae, Cyanophyceae, Chlorophyceae, and Euglenophyceae* (Wetzel, 1983).

A national water quality standard for total phosphorus in freshwater has not been established. While a relatively firm relationship between high phosphorus concentrations and accelerated eutrophication has been established

47

for many lakes, reservoirs, and streams, certain conditions exist in some areas which complicate the establishment of firm criteria. Some water bodies with phosphorus concentrations higher than suggested limits show no signs of eutrophy while others with concentrations of phosphorus lower than suggested limits exhibit eutrophic qualities.

Naturally occurring phenomena may limit plants as nuisances. Turbidity due to suspended inorganic particles may reduce light penetration and thereby decrease the euphotic zone of optimal light for algal and aquatic macrophyte growth. Water body morphology (steep banks, great depth, and high discharge rates) may be effective in reducing nuisance plant growth. Some water bodies are managed for waterfowl or other wildlife and thus more productive communities are desirable. Some studies have shown nutrients other than phosphorus as the limiting nutrient.

EPA *Quality Criteria for Water 1986* (U. S. EPA, 1986), offers a discussion of phosphate phosphorus and discusses some of these problems. Suggested goals for total phosphorus concentrations in freshwater are recommended based on a great volume of work relating phosphorus to eutrophication of lakes, streams, and other water bodies. For streams, where they enter a lake or reservoir, 50 µg/l total phosphorus is suggested as the limit (U. S. EPA, 1986). Within lakes or reservoirs, 25 µg/l is the recommended limit (U. S. EPA, 1986). The goal for prevention of nuisance plant growth in streams an other flowing waters not directly discharging into lakes or impoundments is 100 µg/l total phosphorus (U. S. EPA, 1986). Part of the above goals were developed based

48

on the fact that most uncontaminated lakes have surface water concentrations of total phosphorus in the range of 10 - 30 µg/l (U. S. EPA, 1986).

Vollenweider (1976, in Wetzel, 1983) suggests total phosphorus loading in terms of g/m²/yr critical for eutrophic conditions within the receiving waterway based on water volume and mean depth/hydraulic detention time. Table II summarizes phosphorus loads determined to be "permissible", allowing a water body to remain oligotrophic, and "critical", loads at or above which a water body may begin to show signs of accelerated eutrophication.

TABLE II

VOLLENWEIDER'S SUGGESTED PHOSPHORUS LOADINGS FOR LAKES

(Mean Depth)/ (Hydraulic Detention Time) (m/yr)	Oligotrophic or Permissible Loading (g/m²/yr)	Eutrophic or Critical Loading (g/m²/yr)
0.5	0.07	0.14
1.0	0.10	0.20
2.5	0.16	0.32
5.0	0.22	0.45
7.5	0.27	0.55
10	0.32	0.63
25	0.50	1.00
50	0.71	1.41
75	0.87	1.73
100	1.00	2.00

Source: from Wetzel (1983)

Since phosphate, which is normally available in limited supplies, acts as a

49

fertilizer for aquatic algae and plants, methods for reducing harmful blooms of algae have been attempted. In general, algae are best controlled by limiting the inflow of phosphate for the following reasons (Thomas, 1973):

1. Phosphate is present in only trace amounts in oligotrophic lakes.

2. Natural tributaries running into these lakes contain very little phosphate unless they are subjected to pollution by the influence of man.

3. Fewer phosphate than nitrogenous compounds are washed out of agricultural lands.

4. Rainwater often contains large quantities of nitrogenous compounds that can be utilized by plants.

5. Bacteria and blue-green algae living in lake water are able to fix nitrogen or to produce the growth factors for algae.

6. The addition of phosphate only to lake water is sufficient to increase the growth of bacteria and blue-green algae.

7. Some blue-green algae produce toxins that are very toxic to warm-blooded animals.

8. Nitrogenous compounds from putrefied parts of organisms and sludge return to the biochemical cycle in larger quantities than phosphate compounds.

9. In eutrophic lakes, nitrates are eliminated from time to time by the process of denitrification.

10.   It is relatively less expensive and easier to eliminate phosphates from sewage water (by alum or $FeCl_3$) in the activated sludge process than removing nitrogenous compounds.

Precise levels of phosphate in the environment which are "safe" for humans related to the accelerated eutrophication of lakes have not been determined. A variety of different responses by lakes and streams in different regions to levels of phosphate input compound the difficulty of determining such a number. A number of eminent researchers have developed measures of lake trophic status based in part on the input of phosphates.

Nitrogen

Problems associated with excessive nitrogen in surface waters are primarily associated with eutrophication while high levels of nitrate in drinking water may lead to human health or animal health problems. Control of nonpoint sources of nitrogen is difficult due to the dynamic nature of nitrogen transformations and transport, and the many natural and anthropogenic sources of this element. Sustained high crop production usually requires that nitrogen fertilizers be added to the soil on a short-term basis due to the many avenues of loss and the low crop recovery of nitrogen.

Nitrate poisoning in humans is rare since acute poisoning in an adult requires a single oral ingestion of one to two grams of nitrate as nitrogen, far above the normal exposure episodes. Rather the health effects of nitrate are usually due to nitrite which is formed by reduction of nitrate by intestinal flora in

51

some animals and the human infant during the first three to four months of life.

Nitrite is rapidly absorbed into the blood from the stomach. The toxic effects are

due to the fact that nitrite acts as an oxidant, converting the Fe(2) of hemoglobin

to Fe(3). The oxidized hemoglobin (methemoglobin) cannot transport oxygen.

The high susceptibility of newborns and infants relative to older children and

adults is due to the fact that: 1) nitrate reduction is rapid because of the higher

gastric pH of infants (favors bacterial growth); 2) fetal hemoglobin is more readily

oxidized; and, 3) the activity of enzymes that restore methemoglobin to

hemoglobin is lower in infants. Cyanosis is observed when about 5% of the

hemoglobin is converted to methemoglobin. The observed toxic effects of nitrate

in livestock are qualitatively similar to those in humans, but the dose required to

produce toxicity is often much higher and is dependent on the species and diet.

Nitrate poisoning in livestock is not widespread (Keeney, 1983).

The over-enrichment of surface waters with nutrients, primarily nitrogen

and phosphorus, results in a number of water quality changes which are usually

regarded as undesirable. These effects include increased algal blooms, greater

aquatic macrophyte growth, and dissolved oxygen depletion and are much more

evident in lakes and impoundments than surface waters. Considerable research

has been directed at this problem over the past three decades and efforts to

classify lakes according to their trophic status have been developed by

evaluating nutrient levels, transparency, and algal chlorophyll *a* concentrations.

Most models have been oriented primarily toward phosphorus due to the

finding that phosphorus rather than nitrogen is usually the nutrient limiting lake

52

productivity. This is due in large to the relatively greater mobility of nitrogen compared to phosphorus, and to the uncontrollable sources of nitrogen. However, it is erroneous to assume that all lakes are phosphorus rather than nitrogen limited.

The major combined nitrogen species (organic nitrogen, ammonium ions, and nitrate) in the biosphere are interrelated by a complicated series of chemical and biological reactions referred to as the nitrogen cycle. Key biological transformations are: 1) immobilization or the assimilation of inorganic forms of nitrogen by plants and microorganisms to form organic nitrogen compounds; 2) ammonification or mineralization which is the decomposition of organic nitrogen to ammonium; 3) nitrification, the microbial oxidation of ammonium to nitrite; 4) denitrification, the reduction of nitrate or nitrite to dinitrogen oxide and nitrogen gas; and, 5) nitrogen fixation, the reduction of nitrogen gas to ammonia (Keeney, 1983).

Important chemical reactions in the soil nitrogen cycle are: 1) ammonia volatilization or sorption, the release or uptake of atmospheric ammonia by soils or plants; 2) ammonium exchange, the rapid and reversible exchange of ammonium from soil cation exchange sites to soil solution; 3) ammonium fixation, the entrapment of ammonium in the interlayers of 2:1 clay minerals such that it is only slowly released; and, 4) chemical denitrification, the reaction of nitrite with soil constituents at acid pH or under elevated temperatures to yield nitrogen gas or nitrogen oxides (Keeney, 1983).

Mineralization and immobilization operate as a dynamic equilibrium in

53

unfertilized soils and the amount of inorganic nitrogen in these soils is a function of the relative magnitude of these two opposing processes. As long as conditions are favorable for biological activity, these processes are constantly occurring. Net mineralization (inorganic nitrogen release in excess of that immobilized) often is 2-4% of the total soil N/yr in temperate climates. The net amount of nitrogen mineralized or immobilized in a given time is a function of many factors including type of substrate, temperature, and water and aeration status (Keeney, 1983).

Nitrification transforms the relatively immobile ammonium into nitrate which then can be readily leached, taken up by plants, or denitrified. The two-step nitrification process is almost exclusively mediated by obligate aerobic bacteria. *Nitrosomonas* is considered the most common bacteria for the first step: ammonium - oxygen yields nitrite, water, and hydrogen. *Nitrobacter* is the most common and best known nitrite oxidizer: nitrite plus oxygen yields nitrate. Nitrite is normally oxidized as rapidly as it is formed and does not accumulate except under high pH, high ammonia conditions which are unfavorable for *Nitrobacter* activity (Keeney, 1983).

Denitrification can be a major source of nitrogen loss. It is carried out by bacteria that are adapted to use nitrate or nitrite as a terminal electron acceptor when oxygen has been depleted. In addition to an anaerobic environment, organic matter is essential as a source of electrons and energy. The commonly accepted pathway is nitrate to nitrite to nitrogen oxide to dinitrogen oxide to nitrogen gas (Keeney, 1983).

54

Nitrogen is transported from agricultural lands by erosion, runoff, and leaching. It is difficult to distinguish between these routes on a watershed basis. A host of climatic, soil, topographic, land use, and management factors affect the forms and amounts of nitrogen reaching the receiving waters. The complexity of these factors along with the dynamic nature of the nitrogen cycle greatly complicate modeling of nonpoint source nitrogen pollution from agricultural lands.

In most cases the nitrogen leaving agricultural fields by surface runoff is in the organic form associated with eroded soil. The eroded soil is usually of finer particle size and has more associated organic matter than the bulk soil resulting in an enrichment of the eroded sediment nitrogen content. The ratio of sediment nitrogen to bulk soil nitrogen is the enrichment ratio. Menzel (1980) concluded that this ratio decreases as erosion increases and arrived at values ranging from 2.5 to 7.5 for cropland.

Surface runoff will also contain soluble nitrogen, primarily ammonium and nitrate. The concentrations and export of these inorganic forms are the net result of many factors and thus average values have little meaning. Precipitation adds significant inorganic nitrogen (5-10 kg/ha/yr) and usually more nitrogen is added in precipitation than is lost in surface runoff and baseflow. When precipitation or irrigation begins these two forms are leached into the soil. Ammonium will be retained at soil cation exchange sites, may nitrify, and erode with soil particles or reenter the soluble nitrogen fraction. Nitrate can move through the soil and enter into the soil nitrogen cycle, reappear in surface flow

55

downslope, or be leached to ground water. When precipitation exceeds

infiltration the runoff water can obtain additional inorganic nitrogen from

vegetation (plant residues). The ratio of inorganic nitrogen to total nitrogen tends

to increase as more land in a watershed is in agricultural production (Keeney,

1983).

Nitrate leached below the root zone may end up in interflow, ground

water, or reappear as surface or base flow. In many cropland situations this is

the major path of nitrogen loss. The main processes in the movement of nitrate

in soil are: 1) bulk flow (convection) of dissolved substances in soil solution due

to mass flow of soil water; 2) molecular diffusion due to concentration gradients;

and, 3) hydrodynamic dispersion due to mixing resulting from local differences in

water flow velocity and direction. Soil water flow is caused by a driving force

resulting from a potential gradient, and flow occurs in the direction of decreasing

potential with the rate of flow proportional to the potential gradient and affected

by the geometry of the pore channels. If the soil is saturated with water,

gravitational force dominates and the soil water has a positive pressure potential

as compared to a free water surface. The energy of water in soils is commonly

expressed in bars, which is equivalent to the pressure exerted on a unit area by

a 1020 mm column of water. Most of the water in soils is under matric potential

but some is also acted on by gravitational and osmotic forces. These three

forces combine to form the total potential energy of soil water (Ψ_{tot}). The rate of

flow of water in soils is a result of: 1) the change in water potential per unit of

distance; and 2) the hydraulic conductivity (K) which is the ability of the soil to

transmit water. These factors are related by a form of Darcy's Law: $q=K^* \Psi_{tot}/L$, where q is the rate of flow and L is the distance between the two locations. When the soil is saturated the matric and solute forces are zero, and gravitational potential energy difference is the only driving force. The dominant factor affecting the rate of water movement to a lower position in the soil is the size and continuity of the pores in the soil (Keeney, 1983).

The nitrogen and hydrologic cycles are intimately linked and cannot be considered separately when evaluating control of nonpoint source nitrogen pollution. Suggested methods for the control of nitrogen loss from croplands include: 1) agricultural BMPs which reduce erosion and runoff; 2) efficient use of irrigation to minimize leaching of nitrate from the root zone before plant uptake can occur; 3) consideration of cropping sequences or cover crops that might utilize residual nitrate; 4) improved fertilizer management (timing, rates, evaluation of soil nitrogen availability); 5) use of slow release nitrogen fertilizers for long-season crops; and, 6) use of nitrification and urease inhibitors where appropriate (Keeney, 1983).

Nutrient parameters are of special interest. Historically, attention has been given to phosphorus and nitrogen because they are often limiting nutrients which are necessary for algal growth. Carbon is often found to be particularly abundant and thus attempts to limit excessive algal growth have focused on phosphorus and nitrogen.

Eutrophication is a natural process of lake aging whereby a lake matures from a relatively unproductive oligotrophic status to a highly productive eutrophic

state. Unfortunately, anthropogenic wastes have greatly accelerated this process in many lakes in developed areas. The nutrients nitrogen and phosphorus, abundant in anthropogenic wastes, are not often found in abundance in natural conditions. If anthropogenic activities produce significant quantities of these nutrients, and if they are allowed to enter stream and lake systems, they provide ample nutrients for accelerated growth. As a lake becomes increasingly productive certain species are no longer able to compete and diversity decreases. Accelerated rates of eutrophication of lakes have been attributed to increased amounts of nutrients discharged into waters flowing into the lakes (Warren, 1971). If nutrient levels are left unchecked, their abundance may lead to undesirable water quality conditions. The water quality problems can include reduced diversity of organisms and conditions which are aesthetically undesirable such as extensive algal blooms, reduced water clarity, and offensive odors. If the water body is used as a water supply source, increased cost for water treatment may be required.

Streams can also be adversely affected by increased levels of nutrients. It is certain that enrichment causes changes in the flora and encourages the growth of periphyton and macrophytes. In some areas of the United States there has been a documented decrease in clear-water fish species as a result of nutrient enrichment. These species are often replaced by warm-water species. Additionally, turbidity levels may increase due to increased suspended algae (Hynes, 1970).

58

Precipitation as a Source of Nutrients

The concentration and accumulation of phosphorus by precipitation is small relative to that of nitrogen. No phosphorus gases exist in the atmosphere. The only sources are airborne particulate matters, mostly dust, and a significant portion of that is organic in nature. A significant amount of phosphorus is removed from the atmosphere as dry fallout. Most of the phosphorus in rain is associated with dust. The amount of phosphorus added by precipitation is insignificant compared with that present in soils and fertilizers. The phosphorus loading by precipitation can be significant when compared with concentrations of phosphorus in surface runoff, especially from land not in agricultural production (Tabatabai, 1983 in Schaller and Bailey, 1983). Table III is a summary of estimated concentrations and loadings of phosphorus forms present in precipitation at various locations in the U.S.

Precipitation adds significant inorganic nitrogen (5-10 kg/ha/yr) and usually more nitrogen is added in precipitation than is lost in surface runoff and baseflow (Keeney, 1983). Tabatabai (1983) also estimated the areal loadings of various nitrogen forms from precipitation based on numerous studies. Table IV gives these estimates for various locations in the U.S.

59

TABLE III

AMOUNTS OF PHOSPHORUS DEPOSITED IN PRECIPITATION AT VARIOUS LOCATIONS

State	PO_4 as Phosphorus (mg/l)	Total Phosphorus (mg/l)	PO_4 as Phosphorus (kg/ha/yr)
Arizona	0.002	...	5.8
California	0.019 - 0.670 (0.260)	...	...
Florida	0.019 - 0.024	0.034	0.41 - 1.02[*]
Indiana	0.020 - 0.040	...	...
Iowa	0.089 - 0.259 (00.138)	...	0.71 - 2.07 (1.10)
Minnesota	...	0.028 - 0.060 (0.036)	0.22 - 0.49[*]
Nebraska	0.030 - 0.200 (0.100)	...	0.10 - 1.20 (0.40)
Ohio	0.036	0.027 - 0.190 (0.080)	...
Wisconsin	...	0.021	0.16[*]

[*] indicates total phosphorus. Numbers in parentheses are median values.
Source: from Tabatabai (1983) in Schaller and Bailey (1983)

60

TABLE IV

AMOUNTS OF INORGANIC NITROGEN DEPOSITED
BY PRECIPITATION AT VARIOUS LOCATIONS

State	NH_4 as Nitrogen (kg/ha/yr)	NO_3 as Nitrogen (kg/ha/yr)	Total Inorganic Nitrogen (kg/ha/yr)
Arizona	...	3.5	3.5
Florida	1.2 - 1.5	2.3 - 2.8	3.5 - 4.3
Iowa	3.7-10.9 (7.2)	4.4 - 9.2 (6.1)	9.8 - 17.6 (13.5)
Michigan	2.1 - 3.1	3.2 - 4.0	5.3 - 7.1
Minnesota	...	...	5.8 - 13.6 (8.7)
Nebraska	3.9 - 13.7 (4.9)	1.8 - 5.8 (3.6)	5.7 - 19.5 (8.5)

Numbers in parentheses are median values.
Source: Tabatabai (1983) in Schaller and Bailey (1983)

61

Unit Area Loading

Beaulac and Reckhow (1982) conducted an extensive literature review of nutrient export studies. They reviewed and evaluated the studies based on sampling design criteria and compiled the results according to land use for both total phosphorus and total nitrogen. Land uses identified in their review included row and non-row crops, pasture, mixed agriculture, urban, forest, and feedlots. Ranges of export coefficients for total phosphorus and total nitrogen were determined (Table V).

Vaithiyanathan and Correll (1992) examined the effects of land use on phosphorus transport in forested and agricultural soils of the Rhode River watershed, MD. Total phosphorus export coefficients for forest and agriculture were 0.31 ± 0.07 and 2.41 ± 0.85 kg/ha/yr, respectively. Sharpley et al. (1992) determined phosphorus transport from cropped and uncropped (grass) watersheds in the Southern Plains of the U.S. over a five year period. Export coefficients for grass watersheds ranged from 0.02 to 0.31 kg P/ha/yr, and from 0.29 to 14.9 kg P/ha/yr for cropped watersheds. Dillon and Kirchner (1975) measured export of total phosphorus from 34 watersheds in Southern Ontario over a 20 month period. Export coefficients for total phosphorus ranged from 0.025 to 0.15 kg/ha/yr for forested areas and from 0.080 to 0.37 kg/ha/yr for areas of mixed forest and pasture. Clesceri et al. (1986) derived total phosphorus and total nitrogen export coefficients for land uses of forest, mixed forest and agriculture, and agriculture from data for 17 watersheds in Wisconsin.

62

Forest export coefficients ranged from 0.09 to 0.13 kg P/ha/yr and 3.50 to 3.93

kg N/ha/yr. Mixed land use coefficients ranged from 0.14 to 0.24 kg P/ha/yr and

2.50 to 5.61 kg N/ha/yr. Coefficients for agricultural land uses ranged from 0.11

to 0.30 kg P/ha/yr and 3.24 to 16.4 kg N/ha/yr.

TABLE V

QUARTILE RANGES OF LAND USE/NUTRIENT EXPORT COEFFICIENTS

Land Use	Total Phosphorus (kg/ha/yr)	Total Nitrogen (kg/ha/yr)
Row Crops	0.9 - 5.3	4.0 - 21.8
Non Row Crops	0.6 - 1.5	4.1 - 6.5
Pasture	0.2 - 2.6	2.4 - 10.9
Mixed Agriculture	0.5 - 1.4	9.4 - 25.5
Urban	0.6 - 2.7	4.0 - 11.2
Forest	0.1 - 0.3	2.2 - 3.3
Feedlot	170 - 425	1,580 - 3,425

Source: Beaulac and Reckhow (1982)

Omernick (1977), summarizing data from the National Eutrophication

Survey (1972 - 1975), provides some information specific to the Lake Tenkiller

area for that period. Over the broad range of land uses in the Illinois River Basin

above Lake Tenkiller, mean export coefficients of 0.10 kg/ha/yr for total

phosphorus, and 3.63 kg/ha/yr for total nitrogen were calculated. More general

values for the Central Region of the U.S. were determined by combining data

from watersheds. Regional export coefficients for forest and agricultural land

uses were calculated as 0.124 and 0.19 kg P/ha/yr, respectively, and 3.11 and

63

4.40 kg N/ha/yr, respectively.

In the Final Report for Beaver Lake - Phase I Clean Lakes Feasibility Study (FTN Associates, Ltd., 1992) phosphorus and nitrogen export coefficients were developed for the Beaver Lake Reservoir watershed. Literature including Reckhow et al. (1980) and Omernick (1977) was reviewed in obtaining the estimates export coefficients for land uses including crop, pasture, urban, forest, and other. Coefficients in this study were calibrated using discharge monitoring data from various sites around the lake. The export coefficient for the land use category of pasture was adjusted to equilibrate the results of the unit area loading method with the loadings calculated from discharge data. A summary of the export coefficients used in that report follows in Table VI.

TABLE VI

LAND USE/NUTRIENT EXPORT COEFFICIENTS USED
FOR BEAVER LAKE WATERSHED (AR)

Land Use	Total Phosphorus (kg/ha/yr)	Total Nitrogen (kg/ha/yr)
Crop	0.6	4.22
Pasture	0.2 - 0.65	4.0 - 9.5
Urban	0.6 - 2.0	3.0 - 8.0
Forest	0.025	2
Other	0.045 - 0.05	1.2

Source: FTN Associates, Ltd., 1992

64

Confined Animal Waste Characteristics

Large confined animal production facilities and the large amounts of wastes produced have become a disposal problem. Water pollutants resulting from pastured animal production or application of animal wastes to the land include nitrogen, phosphorus, oxygen-demanding biodegradable substances, and pathogenic organisms. Of these, phosphorus and nitrogen are probably the runoff constituents of greatest significance for water quality since the others are attenuated markedly during transport in lotic systems.

Wastes from confined animal operations are generally concentrated. The significant impact of confined animal wastes can be attributed to the fact that the animals are managed in a relatively small area and their wastes concentrated and distributed over a limited area resulting in a high loading potential. Some wastes are collected in lagoons for biological processing while those from poultry tend to be stored for composting or field spreading. Characteristics of animal wastes vary based on the type of animal. Reddy (1981) in Overcash and Davidson (1981) compiled a set of animal waste characteristics based on research results. Table VII describes some characteristics that can be used in estimating the percent of nutrients in dry organic wastes.

65

TABLE VII

SELECTED CHARACTERISTICS OF ORGANIC WASTES

Waste Type	Percent Dry Basis	
	Nitrogen	Phosphorus
Animal Waste		
Beef	0.60 - 3.7	0.11 - 1.4
Dairy	1.50 - 3.7	0.41 - 0.7
Poultry	1.10 - 6.7	0.80 - 1.8
Swine	1.10 - 6.0	1.0 - 2.5
Sheep	4.0	---
Sewage Sludge	1.0 - 6.0	0.8 - 4.0
Digested Sewage Sludge	1.07	0.34
Digested Municipal Sludge	5.50	---
Plant Residues		
Corn	1.15	0.30
Rice	0.43	0.25
Alfalfa	4.0	0.50
Orchard Grass	2.9	0.50
	Parts Per Million	
Sewage Effluent	15 - 40	0.5 - 40
Swine Lagoon Effluent	224	50

Source: Reddy (1981) in Overcash and Davidson (1981)

Nonpoint Source Pollution

Progress in the control of point sources of pollution to water bodies has resulted in a relative increase in the contribution made by nonpoint sources. Nonpoint source (NPS) pollutants in rainfall induced runoff have become the primary focus in water quality improvements since they are the principal cause of

66

remaining water quality problems. NPS can be best described as those pollutant sources not identified, regulated, or managed as point sources. Generally, NPS pollution is generated from diffuse sources including: runoff from agricultural, silvicultural, and urban land uses; construction and resource extraction; leaks and spills; land disposal of wastes; and atmospheric deposition (U.S. EPA, 1991a).

Novotny and Chesters (1981) identified general characteristics of NPS:

*   NPS discharge into surface waters in a diffuse and intermittent manner, usually associated with some meteorological event;

*   NPSs are impacted from extensive land areas and the pollutant is transported overland to surface waters;

*   NPSs are not readily monitored from the point of origin, nor is the overland path easily identified;

*   Control of NPS pollution should be directed at specific sites with the most feasible operations including land management and conservation practices;

*   NPS cannot be measured in terms of effluent limitations and compliance is generally based on land practices rather than water based technology; and,

*   NPS are related to meteorological events, geologic and geographic conditions which are not readily controlled for pollution abatement.

NPS pollution can be derived from either man-made or natural processes. Natural processes include weathering of geologic materials. Agricultural runoff,

a primary contributor to lake and stream eutrophication, is an example of man-made source of NPS. Nonpoint source discharges are diffuse in nature and primarily occur during rainfall events when storm runoff from the land surface carries sediment, sediment-adsorbed chemicals, and dissolved chemicals into receiving water systems. Dissolved chemicals may also percolate through the soil to interflow regions and ground water and may eventually reappear as surface waters in baseflow.

Nonpoint source pollution is stochastic and dynamic and has multimedia dimensions. It is dynamic in the sense that land uses and configurations change over time making the pollutant mix vary both spatially and temporally. Table VIII describes some nation-wide estimates of the contributions of point and nonpoint sources of specific water pollutants. Over 80% of the discharge of total P and total N to U.S. waterways is attributed to agricultural nonpoint sources.

68

TABLE VIII

U.S. ANNUAL DISCHARGE OF POLLUTANTS TO WATERWAYS IN MILLIONS OF TONS (% OF TOTAL)

Source	BOD$_5$	Total Suspended Solids	Total Dissolved Solids	Total Phosphorus	Total Nitrogen
Industrial	3.8 (29.9)	22.9 (2.1)	132 (21.1)	0.16 (11.7)	0.25 (4.6)
Municipal	2.6 (20.5)	2.7 (0.2)	14.5 (2.3)	0.05 (3.6)	0.50 (9.3)
Total Point Source	6.4 (50.4)	25.6 (2.3)	146 (23.5)	0.21 (15.3)	0.75 (13.9)
Cropland	3.2 (25.2)	479 (43.4)	216 (34.7)	0.43 (31.4)	2.37 (43.9)
Woodland	0.8 (6.3)	97.3 (8.8)	55.4 (8.9)	0.12 (8.8)	0.49 (9.1)
Pasture	0.5 (3.9)	78.8 (7.1)	32.8 (5.3)	0.07 (5.1)	0.34 (6.3)
Range	1.8 (14.2)	424 (38.4)	173 (27.7)	0.54 (39.4)	1.45 (26.9)
Total Agricultural Nonpoint Source	6.3 (49.6)	1080 (97.7)	477 (76.5)	1.16 (84.7)	4.65 (86.1)
Total Point & Agricultural Nonpoint Source	12.7	1100	624	1.37	5.40

Source: After Duttweiler and Nicholson (1983)

Nonpoint Source Modeling

Novotny (in Girgini and Zingales , 1986) describes nonpoint source models and their characteristics. Nonpoint source simulation programs are part of a category of loading models which describe formation of runoff and generation of pollutants from a source area. They can be divided into continuous simulation or event oriented models. They also can be based on the distributed parameter or lumped parameter concept. They range from small field

69

sized application models to large deterministic, process-oriented large watershed

models. Most available models range from the simple application of the

Universal Soil Loss Equation (USLE) to multiple parameter-multiple component

models.

Nonpoint source models fall generally into two categories, screening (unit

loads) planning models, and hydrological assessment models. Screening

models are usually simple tools which identify problem areas in a large basin.

They usually rely on assessment of unit loads of pollution to the various lands

within the basin. Unit load is a simple value or function expressing pollution

generation per unit area and time unit for each typical land use. The concept

provides a simple mechanism and quick answers to pollution problems of large

areas where more complicated efforts would fail due to the enormous amounts of

information required to model many complicated processes. The land/use

pollutant loading is compatible with overview modeling where unit loads are

combined with information on land use, soil distribution, and other characteristics

to yield watershed loadings, or to identify areas producing or causing the highest

amount of nonpoint pollution. Sediment loading functions for agricultural areas

are usually based on the USLE. Use of the unit load presumes that an adequate

inventory of land data is available from maps, aerial surveys, remote surveys,

and local information.

Hydrologic models simulate the behavior of a hydrologic phenomenon in

detail but they do not reproduce the phenomenon itself. Abstract models attempt

to represent the system theoretically in mathematical form. These models

70

replace the relevant features of the system with a set of mathematical relationships.

There are basically two approaches to modeling nonpoint pollution. The most common are the lumped parameter models, while some are based on the distributed parameter concept. Lumped models treat the watershed, or a large portion of it, as one unit. The various characteristics of the unit are then lumped together, often with the use of an empirical equation, and the final form and magnitude of the parameters are simplified to represent the model unit as a uniform homogeneous system. Distributed parameter models divide the system into elements. Each element has uniform system parameters, soils, imperviousness, crop, slope, etc. The mathematical foundation of these models commonly uses the finite difference, or finite element representation of the basic differential equation governing flow and mass continuity and motion in one, two or three dimensions.

Models can be designed to run on an event or continuous basis. Discrete event modeling simulates the response to a watershed to a major rainfall or snowfall event. The principal advantage of event modeling over continuous simulation is that it requires relatively little meteorological data and can be operated with shorter computer run time. The principal disadvantage of event modeling is that it requires specification of design storm and antecedent moisture conditions, or detailed rainfall input, thereby assuming equivalence between the recurrence interval of the storm and the recurrence interval of the runoff. The principal advantage of continuous modeling is that it provides a long-term series

of water and pollutant loadings that can be analyzed statistically as to their frequency. A principal disadvantage of continuous modeling is that it requires long simulation runs, thus it may restrict the number of alternatives that can be efficiently investigated.

Typical components of nonpoint pollution models are (Novotny, 1986, in Girgini and Zingales, 1986):

1)   A surface water generation component which describes the transformation of precipitation into runoff and overland flow components;

2)   Soil and ground water components which describe movement of water through the unsaturated soil zone and into the saturated ground water zone;

3)   Runoff and sediment routing component to obtain runoff flow or pollution histograms from the excess rain and eroded soil routing to the watershed outlet;

4)   Erosion component which estimates soil loss from pervious areas;

5)   Pollutant accumulation and wash-off from impervious areas component estimating pollutant mass; and,

6)   The soil adsorption/desorption component which determines the distribution of adsorbed and dissolved fractions of pollutants in soil solution and runoff.

CHAPTER IV

METHODOLOGY

Autosampler Placement and Sample Collection

To obtain data concerning in-stream phosphorus and nitrogen concentrations during runoff events in the Illinois River Basin, automatic water samplers were placed in the field at four locations within the Oklahoma portion of the basin. Three American Sigma (Model 702), and one Isco (Model 2900) samplers were used. These models are discrete samplers with a capacity to collect a total of 24 individual samples. Using a 12-volt DC power system, the samplers can be programmed to collect up to 500 ml per sample at selected time intervals. Each sampler was equipped with a liquid level actuator to activate the samplers when the stream level reached a predetermined level. The sampling interval was set so that the samplers would collect samples throughout the duration of a runoff event (2 - 3 hours between samples). The samplers were programmed to record the time and date of each sample collected. The last available sample bottle in each sampler was filled with deionized distilled water to serve as an analysis control.

The samplers were located at USGS gaging stations so that reasonably

73

accurate stream discharge measurements could be obtained to correspond with sample concentrations. The four sites chosen were: the Illinois River near Watts, OK (USGS 07195500), Flint Creek near Kansas, OK (USGS 07196000), Baron Fork Creek near Eldon, OK (USGS 07197000), and the Illinois River near Tahlequah (USGS 0716500).

The USGS ADAPS database, which allows a user to obtain 'real-time' stream gage height and discharge at USGS gaging stations, was used to determine when the samplers were activated and when a sampling session was complete, as well as the stream discharge at the times when samples were taken by the automatic samplers. Samples were retrieved within 24 hours after the last sample was drawn and were preserved under ice for transport and storage. Analyses were performed within 48 hours of collection.

Total phosphorus was analyzed using the persulfate digestion method of Menzel and Corwin (1965) as described by Lind (1985). Total nitrogen was analyzed using a persulfate digestion method described by Bachman and Canfield (1991).

Analysis of Historical Water Quality Data

Historical water quality data were obtained from U. S. EPA's STORET database for eight long-term USGS monitoring stations within the Illinois River Basin. The request was formulated to include discharge, nitrogen, and phosphorus data collected by federal and state agencies from water years 1980 through 1993. A list of the USGS gaging stations and their locations is given in

74

Table IX. Mean daily discharge at each of the eight gaging stations were
obtained from the USGS ADAPS database for water years 1980 through 1993.

TABLE IX

ILLINOIS RIVER BASIN USGS WATER QUALITY
MONITORING GAGING STATIONS

Station Identification	Verbal Description	Latitude/Longitude	River Kilometer
USGS 07194800	Illinois River W of Savoy, AR at Hwy 16 bridge	36 06 11/94 20 39	214
USGS 07195400	Illinois River at Hwy 16 S of Siloam Springs, AR	36 08 41/94 29 41	186
USGS 07195500	Illinois River at Hwy 54 N of Watts, OK	36 07 48/94 34 12	171
USGS 07196500	Illinois River at Hwy 62 NE of Tahlequah, OK	35 55 17/94 55 15	90
USGS 07195000	Osage Creek near Elm Springs, AR	36 13 19/94 17 18	16
USGS 07196000	Flint Creek at Hwy 412 near Kansas, OK	36 11 54/94 42 30	4.5
USGS 07196900	Baron Fork Creek at Hwy 59 near Dutch Mills, AR	35 52 48/94 29 11	59
USGS 07197000	Baron Fork Creek at Hwy 51 at Eldon, OK	35 55 16/94 50 18	14

Simple descriptive statistical analyses were computed for each of the
gaging stations for nitrogen and phosphorus concentrations, discharge, and total
nitrogen and total phosphorus loads. Additionally, a statistical software package
called FLUX (Walker, 1987b) was used to estimate nutrient loads at the gaging
stations using a flow-weighting technique. Concentration and discharge data
were matched by date and divided into three strata based on stream discharge
for the entire period of record (WTRs 80 - 93) at each gaging station. The first

75

stratum (low flow) included those observations with stream discharge from zero to one-half of the mean discharge (low flow $\leq \frac{1}{2}Q_\mu$). The second stratum (medium flow) included all those observations with discharge from one-half mean discharge to twice mean discharge ($\frac{1}{2}Q_\mu <$ medium flow $\leq 2Q_\mu$). The third stratum (high flow) included all those observations with discharge greater than twice mean discharge ($2Q_\mu <$ high flow).

A flow-weighted mean concentration method was used to calculate average annual loading. Flow-weighted concentration was calculated as:

$$c_{fw} = c_i \ (Q_\mu / q_i)$$

where

c_{fw} = flow-weighted concentration,

c_i = ith observed concentration,

Q_μ = mean discharge, and

q_i = ith observed discharge.

Flow-weighted concentrations were calculated for all observations within a stratum using the mean discharge (Q_μ) for that stratum. The mean discharge for a stratum was calculated as the sum of all long-term flows in that stratum divided by the number of observations. The mean flow-weighted concentration for each stratum was calculated as the sum of all flow-weighted concentrations in the stratum divided by the number of observations. The average annual load contributed by each stratum was then calculated as the mean flow-weighted

concentration for stratum *i* multiplied by the mean discharge for stratum *i*
multiplied by the percent frequency of observed flows within stratum *i*. Total
average annual load was calculated as the sum of the annual loads of each
stratum.

<div align="center">First-Order Kinetic Assimilation Rates</div>

When stream nutrient fluxes are calculated, to determine loading
quantities at a particular point in a stream system, the water column nutrient
concentration and stream discharge are used. Over a period of time and stream
distance, average nutrient concentrations in the water column may appear to
decrease from an upstream point to a downstream point, assuming no additional
nutrient inputs between the points, due to biological incorporation of nutrients
and particulate settling. The rate for this assimilation can be estimated if in-
stream data are available, and an assumption is made that no significant
additional sources of nutrient pollution enter the stream between the upstream
and downstream points.

Keup (1968) reviewed sources of phosphorus in flowing water on the
basis of origin and quantities, and determined that phosphorus within a stream is
assimilated from the flowing mass by biota and sedimentation. He found this
assimilation rate to be measurable, and estimated the rate of removal using first-
order kinetics as 0.007 per kilometer for the South Platte River (CO), and 0.012
per kilometer for the Pigeon River (NC). Simmons and Cheng (1985) examined
the rate and pathways of phosphorus loss from the Nepean River (AUS).